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4. TITLE AND SUBTITLE Understanding the Mechanism of Ennoblement of stainless steel: A multidisciplinary approach.			5. FUNDING NUMBERS C/G #N00014-95-1-0900 PR # 96PRO-2849	
6. AUTHOR(S) Zbigniew Lewandowski				
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Montana State University Grants & Contracts Montana Hall - 304 Bozeman, MT 59717-3980			8. PERFORMING ORGANIZATION REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words) <p>Ennoblement is a phenomenon exhibited by stainless steel (SS) exposed to natural waters. It is characterized by an approximately 400 mV increase in corrosion potential. This increase in corrosion potential can aggravate pitting corrosion. Biofilms growing on SS surfaces are hypothesized to cause this phenomenon.</p> <p>We expose SS to natural waters. After Ennoblement of the samples occurred, microbial deposits and inorganic surface chemistry were studied using XPS and other surface analytical tools.</p> <p>The major accomplishments of this project were (1) to demonstrate that stainless steel Ennoblement in natural fresh water arises from manganic oxide mineralization, (2) to induce Ennoblement under laboratory conditions using pure cultures of the manganese-oxidizing genus <i>Leptothrix discophora</i>, and (3) to determine that microbially deposited MnO₂ can be electrochemically reduced to Mn²⁺ while Fe⁰ is oxidized; manganese oxyhydroxide, MnOOH, is an intermediate product.</p> <p>These findings open the door to assessing and controlling the corrosive impact of Ennoblement by providing a rational explanation for the phenomenon and by allowing the process to be manipulated under controlled conditions. It is the first step in developing new corrosion resistance strategies for stainless steel and other passive metals and alloys.</p>				
14. SUBJECT TERMS Ennoblement, corrosion, stainless steel, maganese, oxidizing bacteria, biofilm, eletrochemistry, Leptothrix discophora			15. NUMBER OF PAGES 9	
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OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-95-1-0900

PR Number 96PR0-2849

Title of GRANT or CONTRACT

**Understanding the Mechanism of Ennoblement of Stainless Steels: A
Multidisciplinary Approach**

Name(s) of Principal Investigators:

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Name of Organization:

Montana State University

Address of Organization:

Grants & Contracts

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Date Submitted

August 28, 1998

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PART I

OFFICE OF NAVAL RESEARCH PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

PR Number: 96PR0-2849

Contract/Grant Number: N00014-95-1-0900

Contract/Grant Title: Understanding the Mechanism of Ennoblement of Stainless Steels: A Multidisciplinary Approach

Principal Investigator: Dr. Zbigniew Lewandowski

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a. Number of papers submitted to refereed journals, but not published (YET): 2

B.H. Olesen, R.Avcı, Z. Lewandowski Manganese Dioxide as a potential Cathodic reactant in Corrosion of Stainless Steels. Submitted to Corrosion Science

W.H.Dickinson, Z.Lewandowski Electrochemical Concepts and techniques in the study of Stainless Steel Ennoblement. Accepted to "Biodeterioration" Will be published in Volume 9, Issue 1.

b. + Number of papers published in refereed journals (for each, provide a complete citation): 5

Dickinson W.H., Caccavo Jr. F., Olesen B., Lewandowski Z. (1997). Ennoblement of Stainless Steel by the Manganese-Depositing Bacterium *Leptothrix discophora*. Applied and Environmental Microbiology. 63, 2502-2506.

Lewandowski Z., Dickinson W., Lee W. (1997). Electrochemical interactions of biofilms with metal surfaces. Water Science and Technology. 36, 295-302

Dickinson W.H., Lewandowski Z. Geer R.D. (1996). Evidence of Surface Charges During Ennoblement of Type 316L Stainless Steel: Dissolved Oxidant and Capacitance Measurements. Corrosion. 52, 910-920.

Dickinson W.H., Lewandowski Z. (1996) Manganese Biofouling and the Corrosion Behavior of Stainless Steel. Biofouling. 10, 79-93.

Dickinson W.H., Caccavo F., Lewandowski Z. (1966). The Ennoblement of Stainless Steel by Manganic Oxide Biofouling. Corrosion Science 38, 1407-1422.

c. + Number of books or chapters submitted, but not yet published: 0

d. + Number of books or chapters published (for each, provide a complete citation): 1

Little B.J., Wagner P.A., Lewandowski Z. (1997). Spatial relations between bacteria and metal surfaces. Reviews in Mineralogy 35, 123-159.

- e. + **Number of printed technical reports/non-refereed papers (for each, provide a complete citation):** 5
- Lewandowski Z. (1998). Structure and function of bacterial biofilms. Corrosion 98. NACE San Diego, March 1998. Paper No 296.
- Little, B.J., Wagner P.A., Lewandowski Z. (1998) The role of biomineralization in microbially influenced corrosion. Corrosion 98. NACE San Diego, March 1998. Paper No 98.
- Olesen B.H., Avci, R., Lewandowski Z. (1998) Ennoblement of stainless steel studied by X-ray photoelectron spectroscopy. Corrosion 98. NACE San Diego, March 1998. Paper No 275.
- Dickinson W.H., Lewandowski Z. (1996) Manganese Biofouling of Stainless Steel: Deposition Rates and Influence on Corrosion Processes. Corrosion '96. Denver, Co. March 24-29, 1996. NACE, paper No. 291.
- Dickinson W., Lewandowski Z. (1995). Electrochemical and Microelectrode Studies of Stainless Steel Ennoblement. Corrosion'95, Orlando, Fla. March 27-31, 1995. NACE, Paper 223.
- f. **Number of patents filed:** 0
- g. + **Number of patents granted (for each, provide a complete citation):** 0
- h. + **Number of invited presentations (for each, provide a complete citation):** 3
- Spatial relations between bacteria and metal surfaces. Short Course on Geomicrobiology. Mineralogical Society of America. Alta, Utah. October 18-19, 1997
- Electrochemical Effects of Biofilm Colonization of Metal Surfaces. Department of Environmental Engineering. University of Aalborg, Aalborg, Denmark. August 28, 1997.
- The Role of Manganese Bacteria in Microbially Influenced Corrosion. International Association on Water Quality (IAWQ). International Workshop on Biofouling and Biocorrosion. 10-11 September 1998. Pretoria, South Africa.
- i. + **Number of submitted presentations (for each, provide a complete citation):** 6
- Little, B.J., Wagner P.A., Lewandowski Z. The relationship between biomineralization and microbiologically influenced corrosion. Latin American Biodeterioration Symposium, LABS 3. Florianopolis, Brazil, 27-30 April 1998.
- Lewandowski Z. (1998). Structure and function of bacterial biofilms. Corrosion 98. NACE San Diego, March 1998.
- Little, B.J., Wagner P.A., Lewandowski Z. (1998) The role of biomineralization in microbially influenced corrosion. Corrosion 98. NACE San Diego, March 1998.
- Olesen B.H., Avci, R., Lewandowski Z. (1998) Ennoblement of stainless steel studied by X-ray photoelectron spectroscopy. Corrosion 98. NACE San Diego, March 1998.
- Dickinson W.H., Lewandowski Z. (1996) Manganese Biofouling of Stainless Steel: Deposition Rates and Influence on Corrosion Processes. Corrosion '96. Denver, Co. March 24-29, 1996. NACE.
- Dickinson W., Lewandowski Z. (1995). Electrochemical and Microelectrode Studies of Stainless Steel Ennoblement. Corrosion'95, Orlando, Fla. March 27-31, 1995. NACE.

- j. + **Honors/Awards/Prizes for contract/grant employees (list attached):** 1
 (This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
- k. **Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:** 1 FTE
 Graduate Students: 1 FTE
 Post-Doctoral Associates: 0
 including the number of,
 Female Graduate Students: 0
 Female Post-Doctoral Associates: 0
 Minority* Graduate Students: 0
 Minority* Post-Doctoral Associates: 0
 Asian Graduate Students: 0
 Asian Post-Doctoral Associates: 0
- l. **Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)**
- Agency: NSF
 Title: Center for Biofilm Engineering, internal project 'Biofilm Structure-Function'
 Fiscal 1997-1998 support (PI Zbigniew Lewandowski): \$214,000
 Total Award:\$16,500,000
 Period of Performance: 4/16/90 - 4/15/2001
 Relationship to ONR Grant:
 Chemical, physical, and physiological heterogeneities within biofilms can influence the electrochemical processes occurring at the interface between a metal and its environment This has well documented consequences for corrosion as exemplified by biologically produced oxygen concentration cells and iron sulfide deposits, and may influence the electrochemical phenomenon of Ennoblement. Research in the Biofilm Structure-Function project focuses on describing the heterogeneities within biofilms and has resulted in oxygen concentration maps, maps of the mass transfer coefficient, and physical models of advective transport within biofilms. An example of how this project can complement the ONR project: by mapping the location of aerobic/anaerobic boundaries, the concerted corrosive influence of aerobic bacteria involved in Ennoblement and anaerobic bacteria such as SRB can be investigated.
- Agency: DOE
 Title: Acceptable Endpoints for metals and Radionuclides: Quantifying the Stability of Uranium and Lead Immobilized under Sulfate reducing Conditions.
 Fiscal 1998 - 1999 support: \$133,728
 Total Award: \$345,491
 Period of Performance 11/1/98 - 10/31/2001
 Relationship to ONR Grant:
 The creation of sulfate reducing conditions to immobilize metals will be tested to remove uranium and lead from dilute aqueous solutions. Relation to the ONR grant: use of microorganisms to control redox reactions involving metals
- Agency: SC Johnson Wax
 Title: Chemical Methods of Improving Biocidal Activity of Hydrogen Peroxide and other Peroxides against Microorganisms in Biofilms
 Fiscal 1997 - 1998: support \$51,000
 Total Award: \$114,000

Period of Performance: 8/1/97 - 7/31/99

Relationship to ONR Grant:

The goal of the project is to identify means of increasing biocidal efficacy of hydrogen peroxide against biofilms. Relation to the ONR grant: none

PART II.

Principal Investigator: Dr. Zbigniew Lewandowski

Phone: (406) 994-5915

ONR Program Manager: Dr. Richard Carlin

Program Objective: To establish the mechanism(s) by which microorganisms alter the rate and/or nature of the electrochemical reactions underlying Ennoblement.

e. Significant results:

As a result of the project we demonstrated :

- 1) that the deposits accumulated on 316 L stainless steel exposed to natural waters contained microbially generated manganese dioxide, MnO_2 :
$$\text{Mn}^{2+} + \text{manganese oxidizing bacteria} \rightarrow \text{MnO}_2$$
- 2) that the microbially deposited manganese dioxide acted as a cathodic reactant, accepting electrons from the underlying metal.
- 3) that the microbially deposited manganese dioxide was ultimately reduced to divalent manganese, and that manganese oxihydroxide, MnOOH , was the intermediate product of this reaction:
$$\text{MnO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{MnOOH}$$
$$\text{MnOOH} + 3\text{H}^+ + \text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}.$$
- 4) that pure cultures of the manganese-oxidizing genus *Leptothrix discophora* induce Ennoblement under laboratory conditions.
- 5) that the following sequence of events is likely:
 - a. manganese oxidizing bacteria deposit manganese oxide on the surface of the metal, according to (1)
 - b. manganese oxide is reduced to divalent manganous ions while the base metal serves as a source of electrons, according to (3).
 - c. divalent manganous ions, products of reaction (3), may serve as a source of manganese ions for manganese oxidizing bacteria in reaction (1), generating a loop stimulated by the oxidation/reduction of manganese.
 - d. cathodic reaction (3) continuously consumes electrons provided by anodic dissolution of the base metal and accelerates corrosion, pitting corrosion in case of passive metals.

f. Summary of plans for next year's work.

N/A

g. Names of graduate students and post-doctoral(s) currently working on the project

Dusty Tripp
Graduate Student
Department of Chemical Engineering
Montana State University
Bozeman, MT

Bo Olesen
Ph.D. Candidate
Department of Environmental Engineering
Aalborg University
Aalborg, Denmark

Wayne.H.Dickinson
PhD Candidate
Department of Chemistry
Montana State University
Bozeman, MT

PART III.

A Power Point file containing viewgraphs and supporting information is included as an attachment with this report. In addition, viewgraphs generated from the Power Point file are included. Additional supporting discussion material for the multi-part and supporting viewgraphs is included below.

Technology Issues:

- Noble shift of E_{corr} to values exceeding +300 mV SCE
- Two to three decade enhancement in cathodic current density at potentials above -200 mV SCE
- $E_{\text{cor}} > E_{\text{pit}}$ increases the risk of pit nucleation
- Enhanced cathodic current impedes repassivation by holding E_{corr} above E_{prot}

Objectives:

- Demonstrate that Ennoblement is caused by microbial deposits
- Define the nature of biofouling deposits on ennobled samples
- Determine the reaction responsible for Ennoblement

Approach:

- Expose stainless steels (SS) to natural waters and study the microbial deposits and inorganic surface chemistry.
- Use pure cultures of target bacteria to demonstrate that Ennoblement is caused by specific microbial-metal interactions
- Use XPS spectra to define the nature of biofouling deposits on ennobled samples

Accomplishments:

- Ennoblement can be induced by *Leptotrix discophora* under laboratory conditions
- The Ennoblement-causing mineral deposited on metal samples is MnO_2
- Microbially deposited MnO_2 can be electrochemically reduced to Mn^{2+} ; manganese oxihydroxide, MnOOH , is the intermediate product

Impact:

- Manganese oxidizing bacteria may be responsible for an important example of microbially influenced corrosion. According to our hypothesis, microbially deposited manganese oxide is subsequently reduced to divalent manganous ions by electrons from the base metal. The anodic aspect of this reaction is metal oxidation; i.e., corrosion of the metal.